Beer's Law Example

This example shows how to compute an extinction coefficient k_λ at a given wavenumber λ using absorbance spectra A_λ of known concentrations c. The Beer's law relationship is $ck_\lambda = A_\lambda$.

The Data

Load the napalm data.

```
clearvars
load pnnl_napalm_data
whos
```

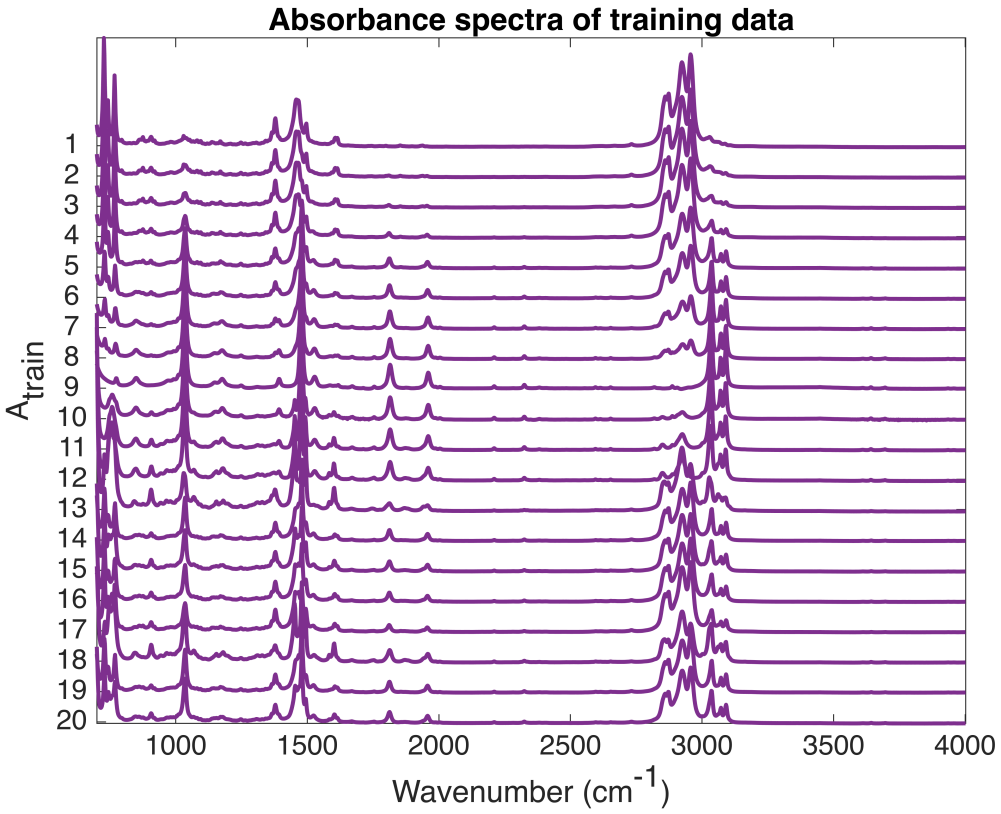
```
  Name                   Size              Bytes  Class     Attributes

  A_train               20x1713           274080  double
  A_unknown             12x1713           164448  double
  C_train               20x3                 480  double
  C_validation          12x3                 288  double
  ConcentrationUnits     1x4                   8  char
  ConstituentNames       1x3                 364  cell
  WavenumberLabel        1x20                 40  char
  Wavenumbers            1x1713            13704  double
  ans                    1x1                   8  double
```

The concentration matrix C_{train} contains the percent by weight of each of 20 solutions in the training data. The columns correspond to benzene, polystyrene, and gasoline.

$$C_{\text{train}} = \begin{array}{c} \begin{array}{cccc} \text{benzene} & \text{polystyrene} & \text{gasoline} & \end{array} \\ \begin{bmatrix} 0 & 0 & 100.0000 \\ 5.1309 & 0 & 94.8691 \\ 10.0660 & 0 & 89.9300 \\ 20.1799 & 0 & 79.8201 \\ 40.0120 & 0 & 59.9878 \\ 59.9972 & 0 & 40.0028 \\ 79.8412 & 0 & 20.1588 \\ 89.8273 & 0 & 10.1727 \\ 100.0000 & 0 & 0 \\ 90.0264 & 9.9736 & 0 \\ 80.1375 & 19.8625 & 0 \\ 64.9950 & 35.0005 & 0 \\ 21.0228 & 45.9197 & 33.0575 \\ 49.9507 & 5.0599 & 44.9895 \\ 40.0182 & 20.0385 & 39.9433 \\ 40.0154 & 10.0036 & 49.9810 \\ 30.0059 & 10.0282 & 59.9659 \\ 40.0340 & 39.9670 & 19.9990 \\ 49.9393 & 3.3748 & 46.6859 \\ 46.6501 & 13.4658 & 39.8840 \end{bmatrix} \end{array} \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 15 \\ 16 \\ 17 \\ 18 \\ 19 \\ 20 \end{array}$$

The absorbance spectra for each of the 20 solutions in the training data are the rows of A_{train}.

```
pnnl_napalm_plot_training_spectra
```

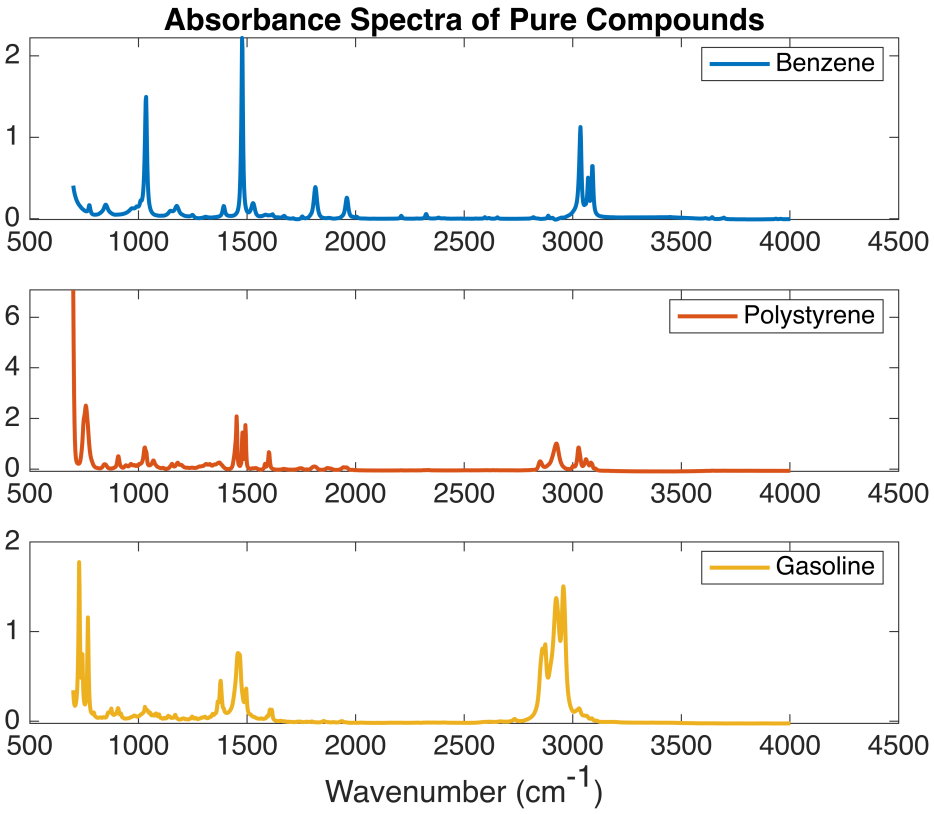


Pure Spectra

Look at the rows of C_{train} and you can see that row 9 is pure benzene and row 1 is pure gasoline. A pure spectra of polystyrene is inferred from a combination of rows 12 and 9.

$$C_{\text{train}}([1, 9, 12], :) = \begin{array}{c} \begin{matrix} \text{benzene} & \text{polystyrene} & \text{gasoline} \end{matrix} \\ \begin{bmatrix} 0 & 0 & 100.0000 \\ 100.0000 & 0 & 0 \\ 64.9950 & 35.0005 & 0 \end{bmatrix} \end{array} \begin{matrix} \\ 1 \\ 9 \\ 12 \end{matrix}$$

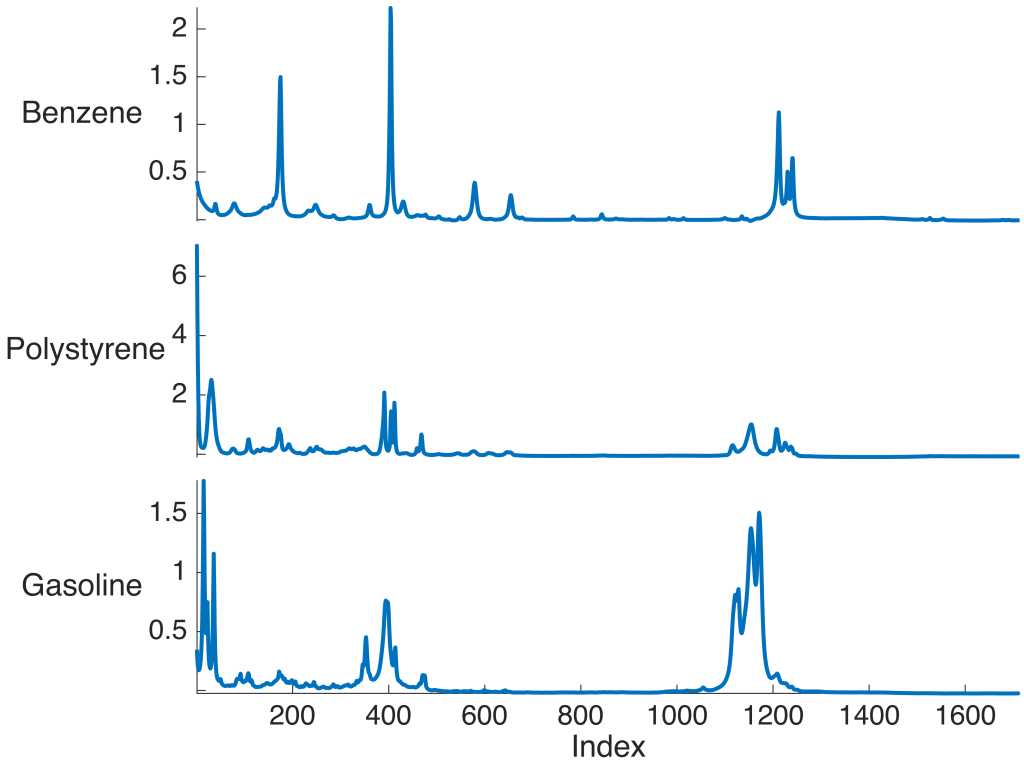
```
A_pure = pnnl_napalm_pure_spectra;
pnnl_napalm_plot_pure_spectra
```



Locate the best index for benzene

Plot the absorbances with `1:m` as the x-axis so you can find the index that corresponds to the best peak for each of the constituents.

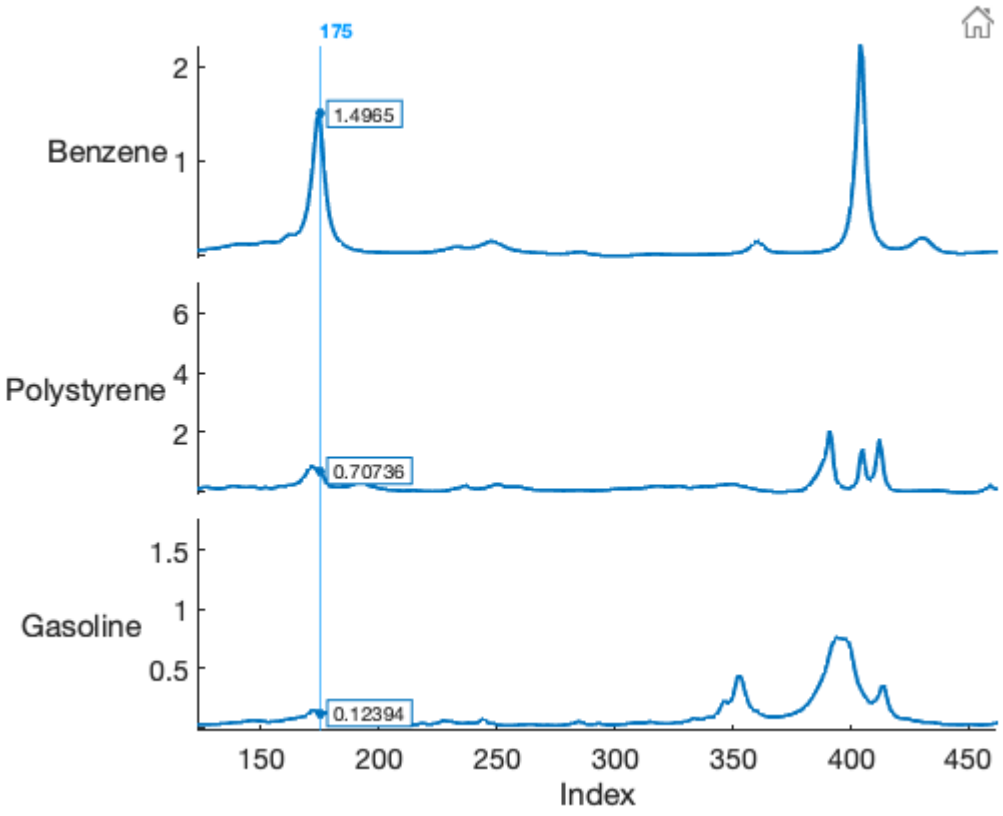
```
m = size(A_pure,2);
figure
stackedplot(1:m,A_pure','LineWidth',2,'FontSize',14,'DisplayLabels',ConstituentNames);
xlabel('Index')
```



Hover over the plot to examine the peaks of the benzene spectrum. The largest peak in the benzene spectrum seems like the natural one to choose, but there are peaks in the other spectra coinciding with the largest peak, so choose the second largest peak to examine. It has index 175. This corresponds to wavenumber $\lambda_{175} = 1035.587$.

```
index = 175;
lambda = Wavenumbers(index)
```

```
lambda = 1.0356e+03
```



Beer's Law for Benzene

Pull out the concentration column for benzene and the absorbtion column for $\lambda_{175} = 1035.587\text{cm}^{-1}$.

```
c_benzene = C_train(:,1);
A_lambda = A_train(:,index);
```

Compute the extinction coefficient $k_{\lambda_{175}}$ for benzene for wavenumber $\lambda_{175} = 1035.587\text{cm}^{-1}$ that best fits the following equation. The fit won't be exact because, for example, looking at the first row there is no value that makes $0 \cdot k_{\lambda_{175}} = 0.1239$ true. However, we can compute a value for $k_{\lambda_{175}}$ that minimizes the sum of squares of the difference $c_{\text{benzene}} \cdot k_{\lambda_{175}} - A_{\lambda_{175}}$ (hence the name "least squares").

$$
\begin{matrix} c_{\text{benzene}} \\ \begin{bmatrix} 0 \\ 5.1309 \\ 10.0660 \\ 20.1799 \\ 40.0120 \\ 59.9972 \\ 79.8412 \\ 89.8273 \\ 100.0000 \\ 90.0264 \\ 80.1375 \\ 64.9950 \\ 21.0228 \\ 49.9507 \\ 40.0182 \\ 40.0154 \\ 30.0059 \\ 40.0340 \\ 49.9393 \\ 46.6501 \end{bmatrix} \end{matrix}
\quad k_{\lambda_{175}} \approx \quad
\begin{matrix} A_{\lambda_{175}} \\ \begin{bmatrix} 0.1239 \\ 0.1801 \\ 0.2207 \\ 0.3423 \\ 0.6381 \\ 0.8222 \\ 1.1272 \\ 1.3174 \\ 1.4965 \\ 1.4311 \\ 1.3286 \\ 1.2203 \\ 0.5492 \\ 0.6973 \\ 0.6603 \\ 0.5863 \\ 0.4573 \\ 0.8525 \\ 0.6905 \\ 0.7131 \end{bmatrix} \end{matrix}
$$

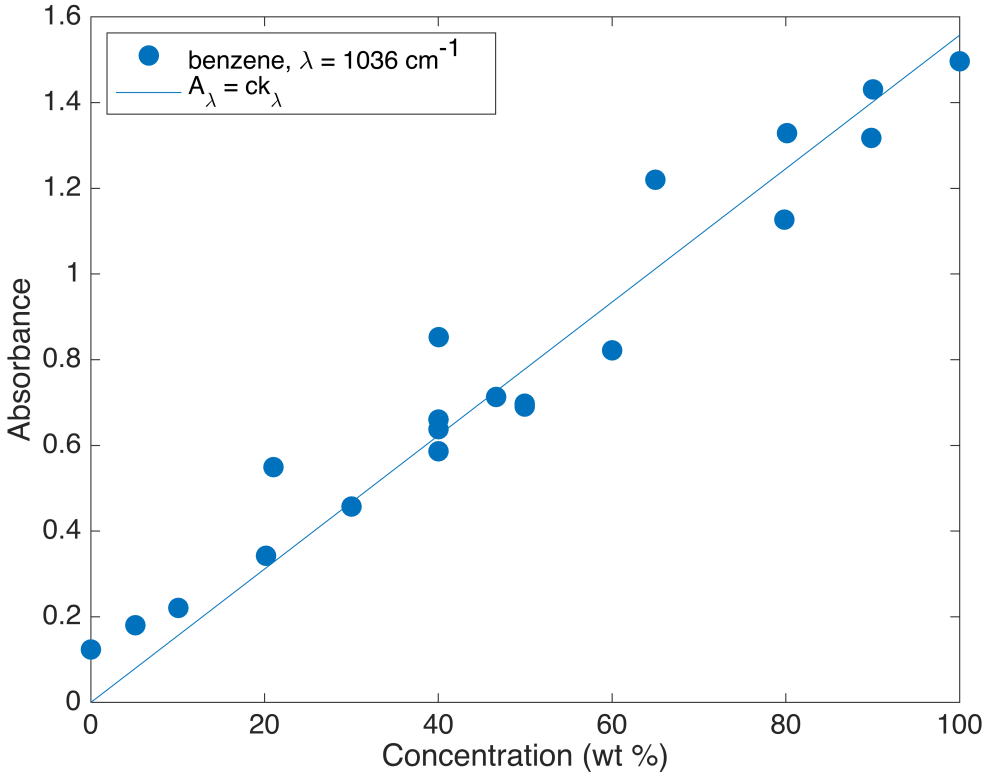
MATLAB's backslash operator computes the least-squares solution to $c_{\text{benzene}} \cdot k_\lambda = A_\lambda$.

```
k_lambda = c_benzene \ A_lambda
```

```
k_lambda = 0.0156
```

Plot the measured absorbtion vs the least-squares best fit $A_\lambda = ck_\lambda$.

```
figure;
plot(c_benzene,A_lambda,'.','MarkerSize',35)
colorOrder = pnnl_colorOrder(1);
hold on
plot(c_benzene, c_benzene*k_lambda,'Color',colorOrder(1,:))
legend(sprintf('benzene, \\lambda = %d cm^{-1}',round(lambda)),'A_\lambda = ck_\lambda
xlabel('Concentration (wt %)')
ylabel('Absorbance')
set(gca,'FontSize',14)
```



Choose peaks for the remaining constituents

Choose bands for each constituent that meet the following criteria:

1. High intensity
2. Don't have high overlap with bands from other constituents.

The following bands for benzene, polystyrene, and gasoline, respectively, met those criteria, but we did not do an exhaustive search. There might be others that are more optimal.

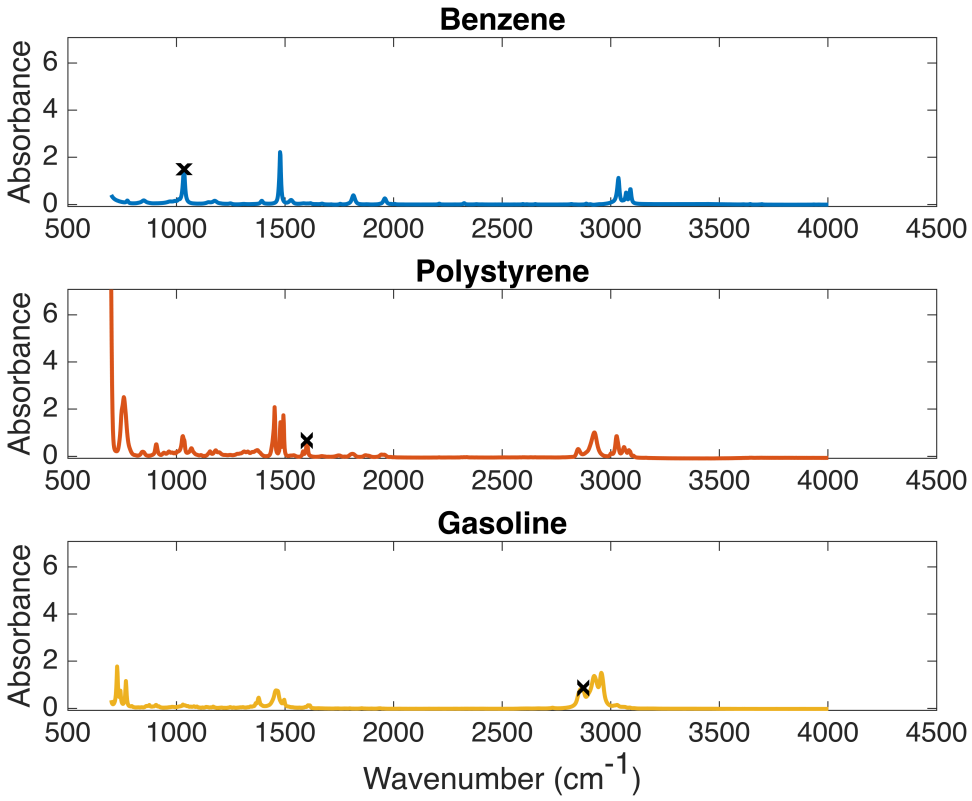
```
wavenumber_index = [175, 468, 1128];
wavenumbers_of_interest = Wavenumbers(wavenumber_index)
```

```
wavenumbers_of_interest = 1×3
10^3 ×
    1.0356    1.6006    2.8734
```

Plot the chosen peaks in each spectra.

```
n = size(C_train,2);
colorOrder = pnnl_colorOrder(n);
figure;
h = gobjects(1,n);
for j = 1:n
    h(j) = subplot(n,1,j);
    plot(Wavenumbers,A_pure(j,:),'LineWidth',2,'Color',colorOrder(j,:));
```

```
    hold on
    plot(Wavenumbers(wavenumber_index(j)),A_pure(j,wavenumber_index(j)),'xk','MarkerSi
    title(ConstituentNames{j})
    ylabel('Absorbance')
end
linkaxes(h)
xlabel(WavenumberLabel)
set(h,'FontSize',14)
```



Repeat for each of the other spectra

Repeat the process for computing extinction coefficients k_λ for each of the other spectra and plot the results.

```
k_lambda = zeros(1,n);
for j = 1:n
    k_lambda(j) = C_train(:,j) \ A_train(:,wavenumber_index(j));
end
```

The extinction coefficients are for benzene, polystyrene, and gasoline respectively.

```
k_lambda
```

```
k_lambda = 1×3
    0.0156    0.0077    0.0098
```

Cross Validation

Cross-validate by running CLS for each of the rows in the training set, leaving one row out, and using that row as the unknown data.

```
p = size(C_train,1);
C_cross_validation = zeros(p,n);
for i = 1:p
    for j = 1:n
        C_cross_validation(i,j) = pnnl_cls(A_train([1:i-1,i+1:p],wavenumber_index(j)),C
    end
end
```

Compute Root Mean Square Errors

```
RMSEC = zeros(1,n);
RMSECV = zeros(1,n);
RMSEP = zeros(1,n);
for j = 1:n
    RMSEC(j) = pnnl_rmse(A_train(:,wavenumber_index(j))/k_lambda(j), C_train(:,j));
    RMSECV(j) = pnnl_rmse(C_cross_validation(:,j), C_train(:,j));
    RMSEP(j) = pnnl_rmse(A_unknown(:,wavenumber_index(j))/k_lambda(j), C_validation(:,j
end
pnnl_display_rmse("Beer's Law",ConstituentNames,RMSEC,RMSECV,RMSEP)
```

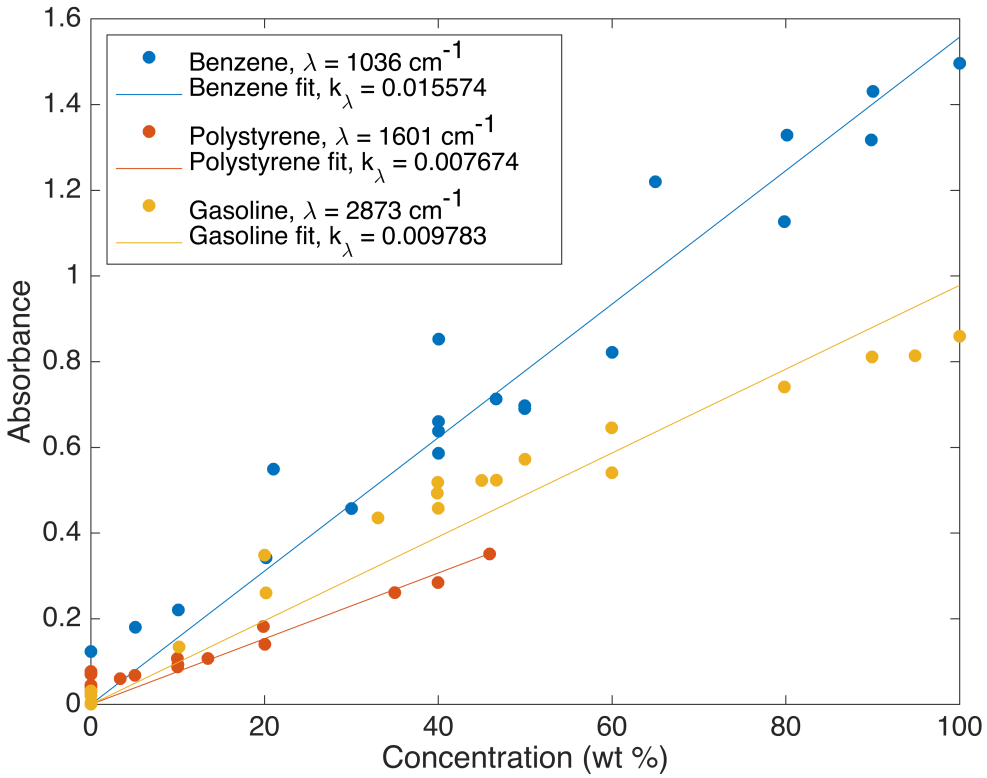
```
------------------------------------------------
Beer's Law       Benzene   Polystyrene      Gasoline
   RMSEC        6.9805        5.6428        8.2886
  RMSECV        7.3288        5.6911        8.8853
   RMSEP        11.019         2.753        25.521
------------------------------------------------
```

Plot the results

Plot the results with lines of best fit.

```
figure;
colorOrder = pnnl_colorOrder(n);
legend_string = cell(1,2*n);
legend_number = 0;
for j = 1:n
    plot(C_train(:,j),A_train(:,wavenumber_index(j)),'o',...
        'MarkerEdgeColor',colorOrder(j,:),...
        'MarkerFaceColor',colorOrder(j,:),...
        'DisplayName',sprintf('%s, \\lambda = %d cm^{-1}',ConstituentNames{j},round(wa
    hold on
    plot(C_train(:,j), C_train(:,j)*k_lambda(j),'Color',colorOrder(j,:),...
        'DisplayName',sprintf('%s fit, k_{\\lambda} = %f',ConstituentNames{j},k_lambda
end
legend('Location','northwest')
xlabel('Concentration (wt %)')
ylabel('Absorbance')
```

```
set(gca,'FontSize',14)
```



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